

# The near-infrared nitric oxide nightglow in the upper atmosphere of Venus

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The  $v' = 0$  progressions of the  $C \rightarrow X$  and  $A \rightarrow X$  band systems of nitric oxide dominate the middle-UV spectrum of the night-time upper atmospheres of the Earth, Mars, and Venus. The  $C(0) \rightarrow A(0) + h\nu$  radiative transition at  $1.224 \mu\text{m}$ , the only channel effectively populating the  $A(0)$  level, must therefore occur also. There have been, however, no reported detections of the  $C(0) \rightarrow A(0)$  band in the atmospheres of these or any other planets. We analyzed all available near-infrared limb observations of the dark-side atmosphere of Venus by the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) instrument on the Venus Express spacecraft and found 2 unambiguous detections of this band at equatorial latitudes that seem to be associated with episodic events of highly enhanced nightglow emission. The discovery of the  $C(0) \rightarrow A(0)$  band means observations in the  $1.2\text{--}1.3 \mu\text{m}$  region, which also contains the  $a(0) \rightarrow X(0)$  emission band of molecular oxygen, can provide a wealth of information on the high-altitude chemistry and dynamics of the Venusan atmosphere.

The luminescence that results from exothermic chemical reactions between the constituents of a planetary atmosphere is customarily termed the night airglow or, simply, the nightglow (1). Although possibly present all day long, it appears most distinctly at night when the other processes of atomic and molecular excitation that depend directly on the action of the Sun are not at play and the diffuse radiation of solar light is at its minimum. The nightglow may originate from various, possibly minor, atmospheric constituents and provides insight into the chemistry, composition, temperature and energy balance of the atmosphere of a planet.

The  $C^2\Pi \rightarrow X^2\Pi$  and  $A^2\Sigma^+ \rightarrow X^2\Pi$  band systems of nitric oxide (often referred to as the  $\delta$  and  $\gamma$  bands, respectively) have long been known in the upper-atmospheric nightglow of the Earth (2, 3) and Venus (4, 5). More recently, they have also been reported in the atmosphere of Mars (6). A common structure, caused by the  $v' = 0$  progression of the aforementioned systems, characterizes the night-time middle-UV spectrum of all 3 planets. Separately and in combination with other nightglow emissions, observations of the nitric oxide nightglow have been used to infer details of the odd-nitrogen chemistry and dynamics in the emitting atmospheres.

In the dayglow, resonance scattering of solar photons from ground-state nitric oxide gives rise to additional  $A \rightarrow X$  ( $v' \geq 0$ ) bands that have been observed on the sunlit side of the Earth (7) but that remain undetected in the atmospheres of Mars and Venus. On Mars, and expectedly also on Venus, the emission of the  $a^3\Pi \rightarrow X^1\Sigma$  system of carbon monoxide is likely to mask the nitric oxide  $A \rightarrow X$  dayglow (8). The fluorescence efficiency of the  $C$  state is low for  $v = 0$  and negligible for  $v > 0$ , presumably due to rapid predissociation (9–12). Day-time observations of the terrestrial atmosphere have found weak  $C \rightarrow X$  ( $v' = 0$ ) bands, which have been attributed to resonance scattering (13–15), although there are significant uncertainties (16).

## Nitric Oxide Deactivation Branching Ratio

The  $C(0)$  level is readily formed by inverse predissociation in the laboratory recombination of unexcited nitrogen and oxygen

atoms (17, 18). The close match between laboratory spectra and nightglow spectra indicates that this is also the mechanism at work in the night-time upper atmosphere.

The  $C(0) \rightarrow X(v'')$  progression constitutes 1 deactivation channel for the electronically excited molecule. The other important deactivation channel is  $C(0) \rightarrow A(0)$ , the production of  $A(v > 0)$  being effectively precluded by Franck–Condon factor considerations (18). The subsequent  $A(0) \rightarrow X(v'')$  progression, together with the  $C(0) \rightarrow X(v'')$  progression, eventually lead to a hot vibrational population in the ground state of the molecule that may be detectable through its middle-infrared emission spectrum (19). At the low pressures in the nightglow region of the atmosphere, collisional quenching of  $C(0)$  and  $A(0)$  is very inefficient. In the absence of other effective production channels, the production of  $A(0)$  is therefore dictated by radiation from  $C(0)$ . In turn, this implies that, in the nightglow, the emission rates for the  $C(0) \rightarrow A(0)$  and  $A(0) \rightarrow X(v'')$  transitions are the same, and that the ratio of the emission rate for  $C(0) \rightarrow A(0)$  to the sum of the emission rates for  $C(0) \rightarrow X(v'')$  and  $C(0) \rightarrow A(0)$  is constant. Estimates of this branching ratio based on laboratory, theoretical, and observational investigations lie in the range 0.21–0.41 (9, 20–26). Some of these studies were adversely affected by contamination or by uncertain calibrations, so a consensus on a precise value has not yet been reached.

Our analysis of the spectrum of both UV progressions published recently (27) provides a new observational determination of the branching ratio. We digitized the published spectrum obtained by the spectroscopy for investigation of characteristics of the atmosphere of Venus (SPICAV) instrument on Venus Express and fit it with synthetic spectra produced with the simulation software LIFBASE (28). The quality of the fit is very satisfactory, even for the weaker bands, as can be seen in Fig. 1. Our best fit leads to a branching ratio of 0.32.

## Near-Infrared Nitric Oxide Band

Although laboratory experiments show that the  $C(0) \rightarrow A(0)$  band should be present along with the  $C(0) \rightarrow X(v'')$  and  $A(0) \rightarrow X(v'')$  progressions, emission in the  $C(0) \rightarrow A(0)$  band has never before been observed in the atmospheres of the Earth, Mars, Venus, or of any other planet. The  $C(0) \rightarrow A(0)$  band comprises  $P$ ,  $Q$ , and  $R$  main branches, with the lines of the stronger  $Q$  branch building up at  $\approx 1.224 \mu\text{m}$  and those of the  $P$  and  $R$  branches spreading on either side toward longer and shorter wavelengths, respectively (30). At moderate to low spectral resolutions, however, the band spectrum looks more like a single line at the position of the  $Q$  branch (20, 31, 32).

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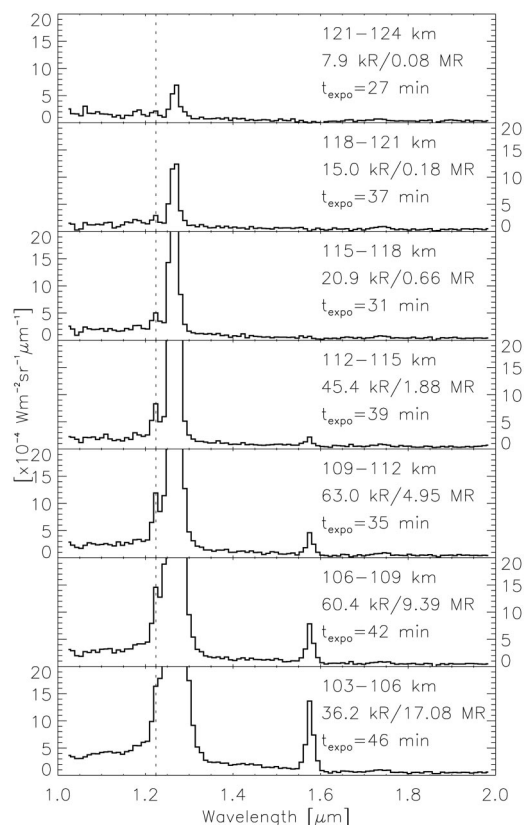
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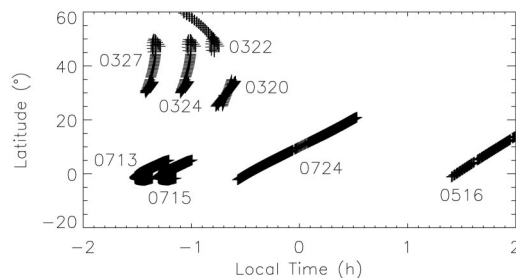


**Fig. 2.** Near-infrared spectra of session 0724.02 (14 April 2008). The position of the nitric oxide  $C(0) \rightarrow A(0)$  band is indicated by the dashed line at  $1.224 \mu\text{m}$ . Estimates for the integrated limb intensity of the  $C(0) \rightarrow A(0)$  band in kilo-Rayleighs were determined by removing the underlying molecular oxygen emission (see text). The stronger emissions centered at  $1.27$  and  $1.58 \mu\text{m}$  are the molecular oxygen  $a(0) \rightarrow X(0)$  and  $a(0) \rightarrow X(1)$  bands, respectively. Estimates for the integrated limb intensity of the  $a(0) \rightarrow X(0)$  band are shown in MegaRayleighs. The estimated ratio of intensities of the 2 oxygen bands is  $63 \pm 6$  (40). In limb viewing, VIRTIS records tens to hundreds of time-sequences of slitwise-resolved spectra. Each spectrum is stored as an entry to a 2-index array. The equivalent exposure time,  $t_{\text{expor}}$ , is evaluated from the number of entries added and the exposure time per spectrum (8 s), and gives a comparative measure of the signal-to-noise ratios in the spectra.

discernible feature at  $1.88\text{ }\mu\text{m}$  in the spectra under investigation rules out the possibility that we are seeing the Meinel system in emission at  $1.22\text{ }\mu\text{m}$ .

The spectrum from session 0724.02 (14 April 2008) in Fig. 2 shows our best example of the near-infrared nitric oxide nightglow in the upper atmosphere of Venus. The limb integrated intensity varies with altitude, reaching a peak somewhere between 109 and 112 km. The trend is consistent with the middle-UV nitric oxide nightglow, a consequence of the optical thinness of the atmosphere for all 3 nitric oxide emissions at these altitudes. Other features apparent in some of the plots are thermal emission from the lower atmosphere leaking through the clouds in the 1.10 and 1.18  $\mu\text{m}$  windows, and subsequently being scattered into the instrument and the  $a(0) \rightarrow X(0)$  band of molecular oxygen at 1.27  $\mu\text{m}$ . On the scale of the figure, the thermal window at 1.74  $\mu\text{m}$  is barely discernible as a gentle undulation. The oxygen  $a(0) \rightarrow X(1)$  band at 1.58  $\mu\text{m}$  is readily apparent below 115 km but is not detectable above.

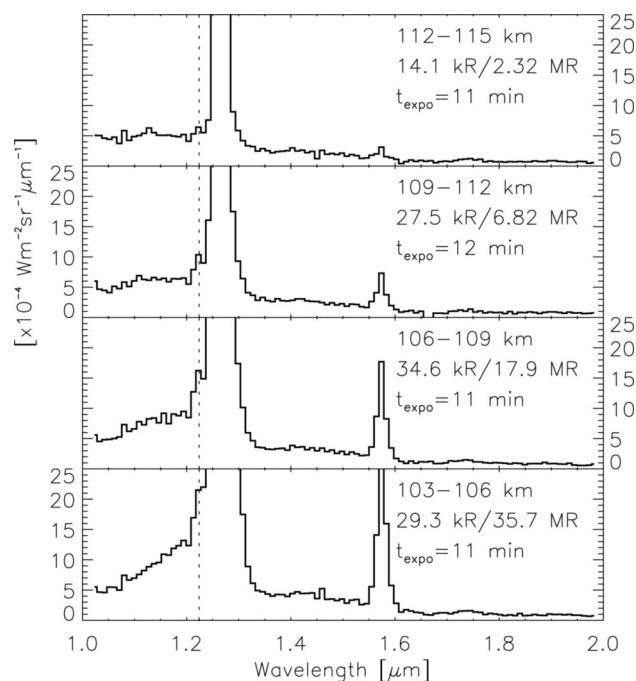
Subtracting the underlying continuum by linear interpolation between the 2 neighbouring pixels, single-pixel radiances in the range  $0.55 \times 10^{-4}$ – $4.41 \times 10^{-4} \text{ W m}^{-2} \text{ sr}^{-1} \mu\text{m}^{-1}$  are obtained for the altitudes quoted in Fig. 2, which translate, according to our



**Fig. 3.** Local time and latitude at the tangent point for the sessions referenced in the present work. The observations in orbits 0713 (3 April 2008) and 0715 (5 April 2008) used a new tracking system that allows for monitoring a fixed region of the atmosphere for a prolonged period.

earlier discussion, into limb intensities of 7.9–63 kR for the  $C(0)–A(0)$  band. At its peak, this implies a total intensity for the middle-UV nitric oxide nightglow of  $\approx 190$  kR, significantly larger than the average value inferred by SPICAV but smaller than the 440 kR that SPICAV observed in orbit 0516 (27). It is clear that session 0724.02 is an episodic event of highly enhanced nightglow similar to those identified by SPICAV. Furthermore, by constructing altitude-averaged composite spectra for sequences of local time/latitude in the orbit, we can confirm that the nightglow is seen throughout the observation session, whose track on a local time/latitude map is displayed in Fig. 3.

Fig. 4 shows spectra from orbit 0516, in which the  $C(0) \rightarrow A(0)$  band appears distinctly at somewhat lower altitudes than in orbit 0724. The inferred peak intensity in the UV is 108 kR,  $\approx 4$  times less than previously reported for this very orbit at an unspecified location north of the equator (27). Factors such as the systematic averaging of individual spectra and the inevitably crude estimate of the  $C(0) \rightarrow A(0)$  band intensities at our instrumental resolution may also contribute to the disparity between the SPICAV and VIRTIS findings.



**Fig. 4.** Near-infrared spectrum of session 0516\_02 (19 September 2007). The position of the  $C(0) \rightarrow A(0)$  band is indicated by the dashed line at  $1.224 \mu\text{m}$ .



A feature at 1.22  $\mu\text{m}$  has also been identified for some latitude-altitude combinations in orbits 0320 (7 March 2007), 0322 (9 March 2007), 0327 (14 March 2007), 0713 (3 April 2008), and 0715 (5 April 2008), with estimated limb intensities  $\approx 10$  kR. A somewhat stronger peak limb intensity,  $\approx 20$  kR, was observed between 30°N and 50°N in orbit 0324. We note that, in the 4 of these latter orbits which were before September 2007, SPICAV detected the nitric oxide nightglow in the middle UV.

## Conclusion

We report 2 unambiguous detections of the nitric oxide  $C(0) \rightarrow A(0)$  band nightglow at 1.224  $\mu\text{m}$  in the upper atmosphere of Venus during orbits 0516 and 0724. This is the first reported observation of this band in a planetary atmosphere. Its observation complements the  $C(0) \rightarrow X(v'')$  and  $A(0) \rightarrow X(v'')$  progressions previously observed in middle-UV spectra of the atmospheres of the Earth, Mars and Venus. The identification has been greatly facilitated by the occurrence of episodes of elevated nightglow emission at nearly equatorial latitudes. For the comparison with PVOUVS and SPICAV measurements, we determined a branching ratio of 0.32 for the ratio of the emission rate for  $C(0) \rightarrow A(0)$  to the sum of the emission rates for  $C(0) \rightarrow X(v'')$  and  $C(0) \rightarrow A(0)$  from a middle-UV spectrum of the Venusian nightglow recently published. The information available from observations of the  $C(0) \rightarrow A(0)$  band is the same

as that available from the  $C(0) \rightarrow X(v'')$  and  $A(0) \rightarrow X(v'')$  bands but the  $C(0) \rightarrow A(0)$  band intensity can be derived simultaneously with the intensity of the  $a(0) \rightarrow X(0)$  band of molecular oxygen from VIRTIS limb observations.

The infrared spectrum of the night-time upper atmosphere of Venus is now known to be quite rich, with the nitric oxide and molecular oxygen nightglow occurring at its short-wavelength end. Both systems originate from the recombination of their constituent atoms, the nitric oxide nightglow through inverse predissociation and the molecular oxygen nightglow through 3-body recombination, but their emission rates peak at different altitudes. The nitrogen and oxygen atoms consumed in these recombination reactions are transported from the sunlit face of the planet, where they are produced, to the night side. It is obviously convenient to simultaneously monitor these 2 contiguous spectral features to help determine the mechanisms and rates of transport, in the horizontal and in the vertical, of the recombining atoms.

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1. Fox JL (1992) in *Airglow and aurora in the atmospheres of Venus and Mars, in Venus and Mars: Atmospheres, ionospheres and solar wind interactions*, eds Luhmann JG, Tatrallyay M, Pepin RO (AGU, Washington, DC) pp 191–222.
2. Cohen-Sabban J, Vuillemin A (1973) Ultra-violet nightglow spectrum from 1900 Å to 3400 Å. *Astrophys Space Sci* 24:127–132.
3. Feldman PD, Takacs PZ (1974) Nitric oxide gamma and delta band emission at twilight. *Geophys Res Lett* 1:169–171.
4. Feldman PD, Moos HW, Clarke JT, Lane AL (1979) Identification of the UV nightglow from Venus. *Nature* 279:221–222.
5. Stewart AI, Barth CA (1979) Ultraviolet night airglow of Venus. *Science* 205:59–62.
6. Bertaux J-L, et al. (2005) Nightglow in the upper atmosphere of Mars and implications for atmospheric transport. *Science* 307:566–569.
7. Barth CA (1964) Rocket measurement of the nitric oxide dayglow. *J Geophys Res* 69:3301–3303.
8. Barth CA, et al. (1969) Mariner 6: Ultraviolet spectrum of Mars upper atmosphere. *Science* 165:1004–1005.
9. Callear AB, Pilling MJ (1970) Fluorescence of nitric oxide. *Trans Faraday Soc* 66:1618–1634.
10. Benoist d'Azy O, López-Delgado R, Tramer A (1975) NO fluorescence decay from low-lying electronic states excited into single vibronic levels with synchrotron radiation. *Chem Phys* 9:327–338.
11. Asscher M, Haas Y (1978) Two-photon excitation of nitric oxide to levels near and above the dissociation limit. *Chem Phys Lett* 59:231–236.
12. Guest JA, Lee LC (1981) Quantitative absorption and fluorescence studies of NO between 1060 and 2000 Å. *J Phys B Phys* 14:3401–3413.
13. Cleary DD (1986) Daytime high-latitude rocket observations of the NO  $\delta$ ,  $\gamma$ , and  $\epsilon$  bands. *J Geophys Res* 91:11337–11344.
14. Cleary DD, Gnanalingam S, McCoy RP, Dymond KF, Eparvier FG (1995) The middle ultraviolet dayglow spectrum. *J Geophys Res* 100:9729–9739.
15. Torr MR, et al. (1995) Thermospheric nitric oxide from the ATLAS 1 and Spacelab 1 missions. *J Geophys Res* 100:17389–17413.
16. Meier RR (1991) Ultraviolet spectroscopy and remote sensing of the upper atmosphere. *Space Sci. Rev* 58:1–185.
17. Young RA, Sharpless L (1962) Excitation of the  $\beta$ ,  $\gamma$ ,  $\delta$ , and Ogawa bands of nitric oxide in the association of atomic nitrogen and oxygen. *Disc Faraday Soc* 35:228–256.
18. Callear AB, Smith IWM (1964) Fluorescence of nitric oxide. *Disc Faraday Soc* 37:96–111.
19. Sun Y, Dalgarno A (1996) Infrared emission spectra of nitric oxide following the radiative association of nitrogen atoms and oxygen atoms. *J Quant Spectrosc Radiat Transfer* 55:245–249.
20. Groth W, Kley D, Schurath U (1971) Rate constant for the infrared emission of the NO( $C^2\Pi \rightarrow A^2\Sigma^+$ ) transition. *J Quant Spectrosc Radiat Transfer* 11:1475–1480.
21. Sharp WE, Rusch DW (1981) Chemiluminescence of nitric oxide: The NO( $C^2\Pi \rightarrow A^2\Sigma^+$ ) rate constant. *J Quant Spectrosc Radiat Transfer* 25:413–417.
22. McCoy RP (1983) Thermospheric odd nitrogen. 1. NO, N( $^4S$ ), and O( $^3P$ ) densities from rocket measurements of the NO  $\delta$  and  $\gamma$  bands of the O<sub>2</sub> Herzberg I bands. *J Geophys Res* 88:3197–3205.
23. Scheingraber H, Vidal CR (1985) Fluorescence spectroscopy and Franck–Condon-factor measurements of low-lying NO Rydberg states. *J Opt Soc Am B* 2:343–354.
24. Tennyson PD, Feldman PD, Hartig GF, Henry RC (1986) Near-midnight observations of nitric oxide  $\delta$ - and  $\gamma$ -band chemiluminescence. *J Geophys Res* 91:10141–10146.
25. Eastes RW, Huffman RE, Leblanc FJ (1992) NO and O<sub>2</sub> ultraviolet nightglow and spacecraft glow from the S3–4 satellite. *Planet Space Sci* 4:481–493.
26. Huestis DL, Slanger TG (1993) New perspectives on the Venus nightglow. *J Geophys Res* 98:10839–10847.
27. Gérard JC, et al. Limb observations of the ultraviolet nitric oxide nightglow with SPICAV on board Venus Express. *J Geophys Res*, 10.1029/2008JE003078.
28. Luque J, Crosley DR (1999) LIFBASE Version 2.0 (SRI International, Menlo Park, CA). Available at [www.sri.com/psd/lifbase](http://www.sri.com/psd/lifbase).
29. Bertaux J-L, et al. (2007) A warm layer in Venus' cryosphere and high-altitude measurements of HF, HCl, H<sub>2</sub>O and HDO. *Nature* 450:646–649.
30. Amiot C, Verges J (1982) Fine structure of the  $C^2\Pi \rightarrow A^2\Sigma^+$  and  $D^2\Sigma^+ \rightarrow A^2\Sigma^+$  band systems of the NO molecule: Homogeneous and heterogeneous perturbations. *Phys Scr* 25:302–311.
31. Ackermann F, Miescher E (1969) High resolution study of the  $C^2\Pi \rightarrow X^2\Pi$  emission bands of the NO molecule. *J Mol Spectr* 31:400–405.
32. Dingle TW, Freedman PA, Gelernt B, Jones WJ, Smith IWM (1975) NO( $C^2\Pi \rightarrow A^2\Sigma^+$ ) emission during the radiative recombination of N and O atoms. *Chem Phys* 8:171–177.
33. Stewart AI, Gérard JC, Rusch DW, Bougher SW (1980) Morphology of the Venus ultraviolet night airglow. *J Geophys Res* 85:7861–7870.
34. Bougher SW, Gérard JC, Stewart AI, Fesen CG (1990) The Venus nitric oxide night airglow: model calculations based on the Venus Thermospheric General Circulation Model. *J Geophys Res* 95:6271–6284.
35. Gérard JC, Stewart AI, Bougher SW (1981) The altitude distribution of the Venus ultraviolet nightglow and implications on vertical transport. *Geophys Res Lett* 8:633–636.
36. Hippler M, Pfab J (1998) Electronic spectroscopy of the C state of the NO by laser multiphoton ionization: rotational structure of the  $C^2\Pi(v'=0) \rightarrow X^2\Pi(v'=0)$  two-photon band. *Mol Phys* 94:313–323.
37. Earls LT (1935) Intensities in  $^2\Pi \rightarrow ^2\Sigma$  transitions in diatomic molecules. *Phys Rev* 48:423–424.
38. Svedhem H, Titov DV, Taylor FW, Witasse O (2007) Venus as a more Earth-like planet. *Nature* 450:629–632.
39. Drossart P, et al. (2007) A dynamic upper atmosphere of Venus as revealed by VIRTIS on Venus Express. *Nature* 450:641–645.
40. Piccioni G, et al. (2008) First detection of hydroxyl in the atmosphere of Venus. *Astron Astrophys* 483:L29–L33.
41. Murphy RE (1971) Infrared emission of OH in the fundamental and first overtone bands. *J Chem Phys* 54:4852–4859.
42. Mies FH (1974) Calculated vibrational transition probabilities of OH( $X^2\Pi$ ). *J Quant Spectrosc Radiat Transf* 53:150–188.
43. van der Loo MPJ, Groenenboom GC (2007) Theoretical transition probabilities for the OH Meinel system. *J Chem Phys* 126:114314.
44. van der Loo MPJ, Groenenboom GC (2007) Theoretical transition probabilities for the OH Meinel system. *J Chem Phys* 127:114314, and correction (2008) 128:159902.